Sulfur Hexafluoride as a Gas-Air Tracer

Amos Turk, Sylvan M. Edmonds, and Howard L. Mark

Department of Chemistry, The City College of the City University of New York, New York, N. Y. 10031

George F. Collins

TRC Service Corp., Hartford, Conn. 06103

■ Sulfur hexafluoride, a useful gas-air tracer, is separated in gas chromatography from other components of moist air on columns of silica gel and activated carbon in series, and is detected by electron-capture analysis in concentrations near 1 p.p.b. This sensitivity can be enhanced at least 2000-fold by freeze-out concentration. The maximum error in calculating the concentration of a diluted gas mixture is calculated on the basis of the fraction recovered in reconcentration. SF_6 backgrounds in air are undetectable except near leakage sources such as transformers. The use of SF_6 as a gas tracer to determine the dilution of a stack effluent gave results that were close to the calculated values.

Halogenated compounds have been shown to be suitable tracers for meteorological studies of moving air masses (Clemons and Altshuller, 1966; Collins, Bartlett, *et al.*, 1965; Saltzman, Coleman, *et al.*, 1966). SF_6 is particularly useful because it is amenable to ultrasensitive analysis by electron-capture detection, is convenient to handle and dispense into air, is odorless and nontoxic, is chemically and thermally stable, and does not usually occur in significant concentrations in outdoor air.

The present study describes a procedure for SF_6 analysis that is applicable to moist samples, a concentration procedure that enhances analytical sensitivity, a method of evaluating errors in dilution systems that is particularly relevant to problems of validating gas calibrations at very high dilutions, an examination of SF_6 atmospheric backgrounds, and an outdoor exercise in which SF_6 is used as a tracer of gas diffusion from a real stack.

Analytical Procedures

Sampling. A 1000-cu. inch stainless steel tank was provided with needle valves at both ends, a pressure gage at one end, and a constant differential-type flow controller at the other. The tank was evacuated in the laboratory, and was brought to the field for sampling. In comparative studies, the valve was opened in the field for a fixed time (usually 20 minutes) to permit control of the sample size. The partially evacuated tank was then brought back to the laboratory and pressurized with purified air to 45 p.s.i.g. Extreme precaution must be taken to avoid contamination of the sample with extraneous SF_6. In a laboratory where SF_6 is handled and may find its way into the air supply, the air used for pressurizing the tank should be filtered successively through Drierite, activated charcoal cooled with dry ice–acetone, and silica gel cooled with liquid oxygen. As an additional precaution, a partially evacuated tank must not be stored near a supply of SF_6.

Analysis. A Perkin-Elmer Model 810 gas chromatograph with electron-capture detector and ionization detector amplifier was used. Samples were introduced by connecting the pressurized sampling tank directly to the gas sampling valve and using the 5-ml. loop. The columns were 1-meter × $^1/_8$-inch silica gel and 1-meter × $^1/_8$-inch activated charcoal in series. Neither column alone would separate the sulfur hexafluoride from the three interfering substances in air: oxygen, carbon dioxide, and water vapor. The columns were maintained at 120° C. and the detector at 150° C. Prepurified nitrogen was passed through the system at a flow rate of 60 ml. per minute. Under these conditions, the sulfur hexafluoride emerged from the columns after 4 minutes, well separated from the interfering substances. A typical trace obtained from a 5-ml. gas sample is shown in Figure 1.

At the higher sensitivity settings of the ionization detector amplifier, electrical noise in the system was found to be excessive, and a filter consisting of a 3000-ohm resistor and a 10-μf. capacitor was placed between the output terminals of the ionization detector amplifier and the input terminals of the recorder. This decreased the noise to the point where the minimum detectable amount of sulfur hexafluoride was decreased by a full order of magnitude. More filtering was found to be undesirable, as it affected the shape and height of the peak, thus effectively lowering the sensitivity of the system.

Using this setup, sensitivities to about 1 p.p.b. of SF_6 in air were obtained. Figure 2 shows one of the calibration curves. SF_6-air mixtures for calibration were made up by the double dilution system previously described (Collins, Bartlett, *et al.*, 1965). The calibration sample was transferred from the

dilution system into a stainless steel tank, and then was pressurized with air that had been purified as previously described.

This analytical procedure is suitable for routine use with ambient air samples taken under conditions of typical New York or Connecticut summer temperatures and humidities. The moisture is retained on the silica gel column during the analysis of as many as about 50 5-ml. samples. Under these circumstances, reconditioning of the column for removal of water can be programmed during the night without encroaching on the time used for analysis.

Concentration Procedure

For SF_6 concentrations less than about 1 p.p.b., the direct technique described above is not sufficiently sensitive. In such cases, the analytical signal can be recovered by concentrating the SF_6 in several liters of sample into a small volume. To do this, the 5-ml. stainless steel sampling loop of the gas sampling valve is bent into a U-shape so that when it is immersed in refrigerant contained in a Dewar flask, it serves as a freeze-out trap. The inlet and outlet of the gas sampling valve are fitted with needle valves so that the sampling loop can be sealed off. The outlet is also fitted with a rotameter and a wet-test meter. The pressurized tank is then connected as previously described. After flushing the trap several times with the sample, both needle valves are closed and the trap is cooled with liquid oxygen (not liquid nitrogen, which will lead to dangerously high pressures when the trap is warmed). The valves are then opened, and the sample is passed through the trap at a maximum rate of 500 ml. per minute. If this rate is exceeded, not all the SF_6 in the sample is condensed. Since a 1000-cu. inch tank pressurized to 45 p.s.i.g. will release more than 40 liters of sample, this concentration procedure will allow sensitivities of more than 2000 times the direct method of analysis. The wet-test meter measures the total sample. When the desired sample volume has been concentrated, the needle valves are again closed, the loop is warmed with water, and the sample is introduced into the chromatograph.

This concentration procedure is independent of the chro-

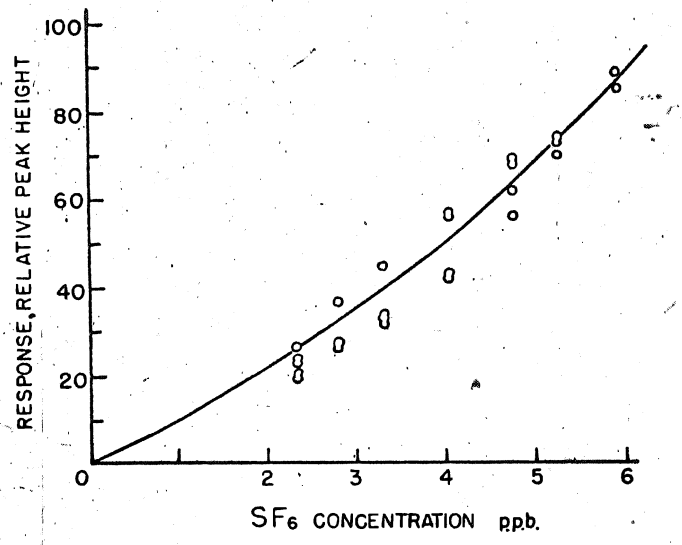

Figure 2. Calibration curve for SF_6 in air

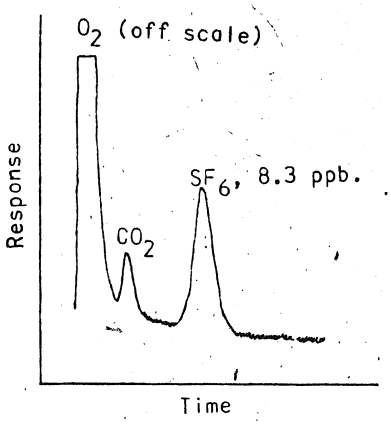

Figure 1. Typical response from mixture of SF_6 and air

Approximate SF_6 concentration, 8 p.p.b.

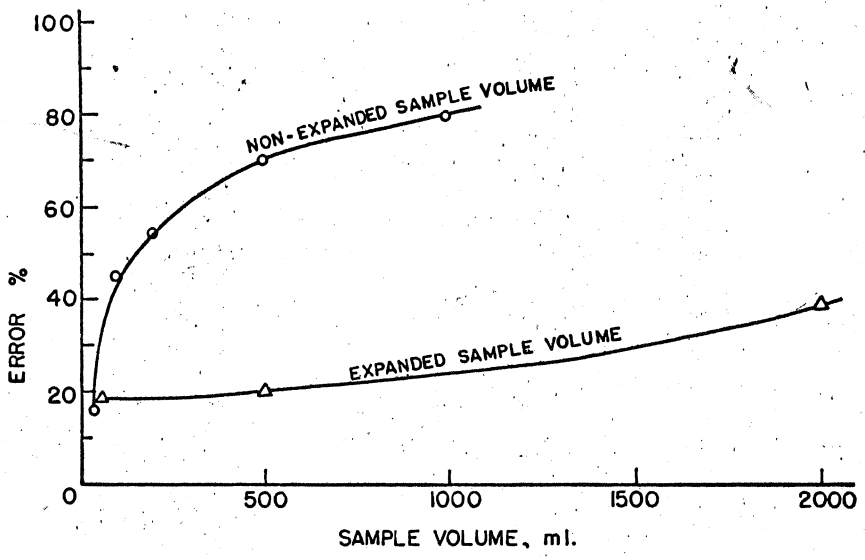

Figure 3. Calculated maximum errors in concentration procedures

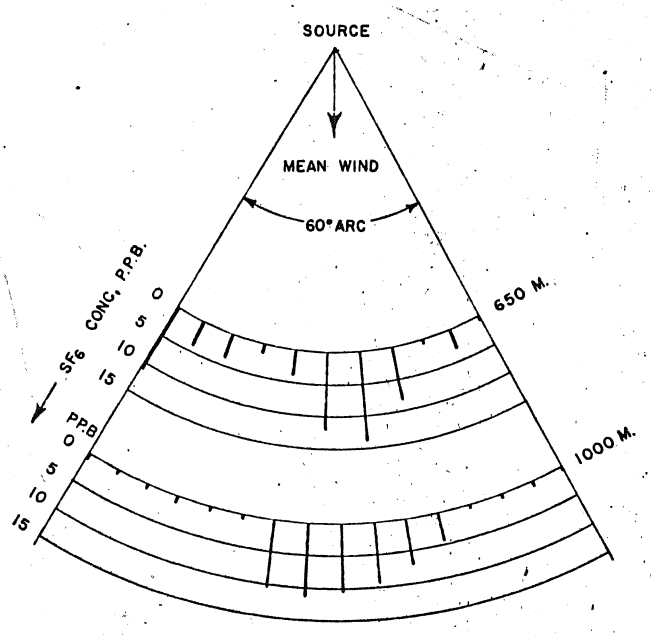

Figure 4. Plume profile during field test

matographic system, and can therefore be used to enhance the response of any analytical procedure for SF_6.

Recovery Analysis

The maximum error in a dilution procedure can be calculated on the following basis. Assume that an initial concentration of vapor, C_i, is sufficiently high so that it can be determined accurately by a reliable method of analysis. The vapor is then diluted by a factor, F_d, that is nominally determined by volume or flow ratios in the system, to a lower concentration, C_d. Now, using some method such as freeze-out trapping, the diluted vapor is reconcentrated by a factor, F_r, to recover a high concentration, C_r, which, like C_i, can be determined accurately. Now the value for the concentration of the diluted vapor that is calculated without a confirming analysis from the applied dilution factor is

$$C_{d(\text{calcd})} = C_i F_d$$

The reconcentrated value is

$$C_r = C_d F_r, \text{ and } C_d = C_r/F_r$$

Now, the error in measuring C_d is

$$\text{Error (fractional)} = \frac{C_{d(\text{calcd})} - C_d}{C_{d(\text{calcd})}} = \frac{C_i F_d - C_i/F}{C_i F_d}$$

$$= 1 - \frac{C_r}{C_i F_d F_r}$$

If $F_d = 1/F_r$—that is, if the original concentration is nominally restored after dilution—then error $= 1 - C_r/C_i$. In this calculation, recovery of the diluted vapor is assumed to be complete, and all of the error is assumed to lie in the dilution

Table I. SF_6 Background Concentrations in Manhattan[a]

Locations near Power Station	Concentration, P.P.B.
On roof of church on south side of 13th Street, midway between C and D	0.09
Power station control room	0.07
North side of 13th Street between Avenues C and D, near D	0.40
North side of 13th Street between Avenues C and D, near C	0.01
On top of transformer in approximate center of power station	0.06
Northeast corner of 13th Street and Avenue D	0.00
Southeast corner of 14th Street and Avenue D	0.06
Locations not near Power Station	
5th Avenue between 54th and 55th Streets	0.01
In Central Park at about 60th Street	0.01
In Central Park at about 82nd Street	0.00
Southwest corner of 106th Street and 5th Avenue	0.00
103rd Street and Riverside Drive	0.00

[a] Container backgrounds may be as high as 0.01 p.p.b.

procedure. If some loss occurring during reconcentration is thus erroneously ascribed to the dilution, then the calculated dilution error is too high. There is no way to resolve the question except to state that the calculated error is a maximum value, and that the real error therefore cannot be any greater than that obtained by this procedure.

Data obtained from the application of this recovery analysis to the concentration technique described are illustrated by the upper curve of Figure 3. The probable cause of these extreme errors was determined to be loss of sample through leaks in the gas sampling valve due to a pressure increase in the valve when the concentrated sample is rewarmed. To minimize this loss of sample, the concentration procedure was modified by providing an 8-ml. expansion chamber that decreases the pressure buildup on the valve. The result is a sharply decreased loss of sample, as is shown by the lower curve of Figure 3. The important point is that if the recovery analysis had not signaled the loss, it would not have been detected or remedied. These curves do not extrapolate to zero error, indicating another loss of sample, comparatively independent of total pressure. The source of this loss might be adsorption on the walls of the container.

SF_6 Backgrounds

Sulfur hexafluoride is used industrially as an insulating material in high voltage transformers and circuit breakers. Therefore, background levels should be checked when work is contemplated near sites where such units are likely to be found. For example, samples were taken near the Consolidated Edison power plant located in Manhattan, New York, N. Y., at 14th Street between Avenues C and D, where SF_6 is used as an insulator for circuit breakers. The results of these tests are listed in Table I. Other samples taken at random locations in Manhattan are also shown. The backgrounds, especially near the power station, are sufficiently high to be a problem if tracing is done over any considerable distance, where large dilutions and consequent low concentrations can be expected.

Another problem inherent in the concentration technique is sorption and desorption of SF_6 on the walls of the container. New containers, never used for SF_6, are free of any contamination .Previously exposed containers, however, can be a source of SF_6 backgrounds. Glass is an offender in this respect, the persistent steady-state concentration from previously contaminated glass being greater than 13 p.p.b. This high value makes glass completely unsuitable for static retention of SF_6 (although it is suitable for dynamic systems). Saran bags gave responses of approximately 0.2 p.p.b., making them suitable containers for re-use if the tracing is done at sufficiently high levels. Stainless steel tanks gave the lowest concentrations of all the materials tried; approximately 0.01 p.p.b. This allows for almost a 100-fold increase in sensitivity by concentrating the sample. The stainless steel containers are most conveniently cleaned by flushing them with air that has been purified in the manner previously described. The flushed containers are then evacuated.

Gas Tracing of a Stack Effluent

The SF_6 tracer method was used in a test of stack effluent dilution conducted on February 17, 1966, in Barrington, N. J., in cooperation with the N. J. State Department of Health and the Owens-Corning Fiberglas Corp.

Test Site. The tracer source was an industrial stack, rising from a roof at 18 meters to a height of 41 meters above ground level (see Figure 4). Stack gas emission rate was 4070 cu. meters per minute, emerging at a temperature of 135° F. and an exit velocity of 1400 meters per minute.

Meteorological Conditions. The weather was clear. The average wind speed was 14 knots, with occasional gusts to 29 knots; the average wind direction was 304 degrees, with a range of 260 to 330 degrees. Atmospheric stability was close to neutral, there being no temperature change with elevation. Under the prevailing conditions, the plume was immediately deflected downward because of the aerodynamic downwash caused by an adjacent structure. The average point of plume touchdown was estimated to be about 4 stack heights from its source, or about 170 meters.

SF_6 Tracer Gas Injection. Tracer gas was injected from 8:40 A.M. to 9:24 A.M. into a $^3/_8$-inch line which ran from the SF_6 cylinder, through a rotameter at roof level, and to a point of penetration about halfway up the stack. The rate of gas introduction into the stack was 0.1325 cu. meter per minute, corrected for 40° F. and a back pressure of 15 p.s.i.g.

Sampling and Analytical Findings. Samples were collected at each of 27 stations (Figure 5) from approximately 9:00 A.M. to 9:20 A.M. during the passage of the SF_6 cloud. The stations were uniformly distributed along each of two 60°

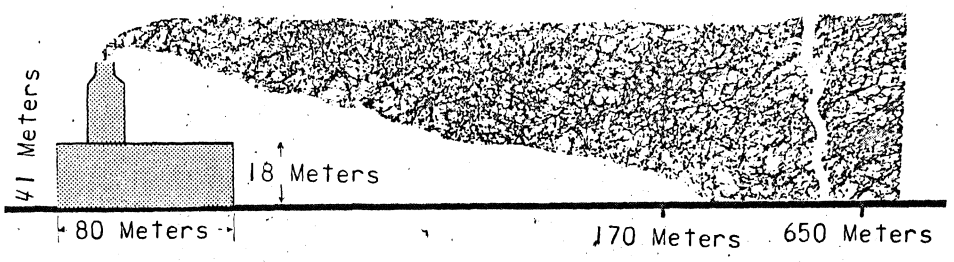

Figure 5. Dispersion of SF_6 discharge from stack during field test

arcs, symmetrically oriented along the plume center line, one at 650 meters and the other at 1000 meters from the source. Samples were collected in 1000-cu. inch stainless steel tanks equipped with valves and constant differential-type flow controllers. Samples were collected 2 meters above ground level over the entire 20-minute period at the uniform rate of 0.028 cu. meter per hour. The results of the SF_6 analyses shown in Figure 5 present a rational dispersion pattern with the exception of some high values at one side of the inner arc, which might have been the result of a puff detached from the main cloud. The plume centerline is delineated well. The average ground level concentration of SF_6 along the plume axis at 650 meters from the source was 14.2 p.p.b. The concentration in the stack was 32,500 p.p.b. Hence, the dilution factor was 2290.

Comparison of Results Obtained from Gas Tracer with Meteorological Calculations.

$$\text{Concn. of } SF_6 \text{ in stack} = \frac{SF_6}{\text{total effluent}}$$

$$= \frac{0.1325 \text{ cu. meter per min.}}{4078 \text{ cu. meters per min.}} \times 10^9$$

$$= 32{,}500 \text{ p.p.b.}$$

Observed dilution factors, referred to plume center line:

$$\text{Dilution factor} = \frac{\text{stack concentration}}{\text{observed downwind concentration}}$$

$$\text{(At 650 meters)} = \frac{32{,}500 \text{ p.p.b.}}{14.2 \text{ p.p.b.}} = 2290$$

$$\text{(At 1000 meters)} = \frac{32{,}500 \text{ p.p.b.}}{11.1 \text{ p.p.b.}} = 2930$$

The downwind ground level concentrations at plume centerline was computed from the equation of Pasquill (1962).

$$\text{Concn.} = \frac{Q}{2\pi\bar{u}\sigma_y\sigma_z} e^{-1/2H^2/\sigma_z^2}$$

where Q = emission rate of SF_6 (cu. meters per second)

$\bar{u}$ = average windspeed (meters per second)

σ_y, σ_z = lateral and vertical diffusion parameters (meters)

H = stack height (meters)

Assuming a straight line distance from the stack to the centerline of the plume on the 650-meter arc, the solution of the equation gives:

$$\text{Concn.} = \frac{0.0022}{2\pi(8.0)(58)(35)} e^{-1/2(41)^2/(35)^2} = 21.4 \text{ p.p.b.}$$

Observed value at 650 meters = 14.2 p.p.b.

From similar calculation at 1000 meters,

Calculated concn. of SF_6 = 12.0 p.p.b.

Observed value at 1000 meters = 11.1 p.p.b.

In predictions of this type, results within a factor of two of the calculated value are considered excellent.

Literature Cited

Clemons, C. A., Altshuller, A. P., *Anal. Chem.* **38,** 133 (1966).
Collins, G. F., Bartlett, F. E., Turk, A., Edmonds, S. M., Mark, H. L., *Air Pollution Control Assoc. J.* **15,** 109 (1965).
Pasquill, F., "Atmospheric Diffusion," Van Nostrand, Princeton, N. J., 1962.
Saltzman, B. E., Coleman, A. I., Clemons, C. A., *Anal. Chem.* **38,** 753 (1966).

Received for review August 7, 1967. Accepted December 22, 1967. The main portion of this work was supported by a research grant from the Division of Air Pollution, U. S. Public Health Service. The field test was supported by the Owens-Corning Fiberglas Corp., with the cooperation of the New Jersey State Department of Health.